

A Study of the Electronic Structure of V_xC_{60} Complex Films by XES and XAS

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V_xC_{60} co-deposited films have been studied by X-ray absorption and emission spectroscopies (XAS and XES) at different V content x ($x=1.0$, 4.4 and 5.4) in the films with respect to possible V_xC_{60} compound formation. In addition, pristine C_{60} and vanadium carbide spectra were recorded for comparison. In the absorption spectra the same peaks are observed as in pure C_{60} up to vanadium content $x=5.5$, which was the highest used in our experiments. However, the decreasing relative π^* absorption intensity (with respect to the σ^* energy region) can suggest partial charge transfer from the metal 3d states to the lowest unoccupied molecular orbital (LUMO) of C_{60} with π^* symmetry. The detuned XES spectra, excited slightly (1.6 eV) under the 1s - LUMO absorption resonant peak indicates a partial symmetry breaking from the interaction between C_{60} and vanadium.

Introduction

Fullerene chemistry has been a very active field since the advent of buckminster fullerene in 1990¹. In metal-fullerene compounds it has been found out that the metal atoms can be bonded in different geometries. The alkaline and alkaline earth metals and mercury are the only metals that have proved to make stable compounds with C_{60} (also predicted theoretically as long as the ionic model can be applied). More recently, some evidence indicating a compound

formation for transition metals has been published^{2, 3}. We tried to study the electronic structure of vanadium fulleride films.

Experimental

The films were produced by co-evaporating C_{60} and on a **Si** substrate in a UHV-grade vacuum system. The XAS spectra were recorded in total electron yield (TEY) mode, with a 0.3 eV resolution, measuring the sample current. The XES spectra were taken using a grazing incidence spectrometer using spherical grating (5 m radius, 400 lines/mm) grazing incidence x-ray spectrometer with a 2D detector. The spectrometer as well as the monochromator resolution was set to about 0.6 eV during the carbon *K* emission measurements.

Results and discussion

The XAS spectra show differences in the σ^* absorption region with varying V content in the films; higher V content gives stronger σ^* absorption. (with electron transfer from the metal (3d levels), the LUMO π^* orbitals (t_{1u}) are being partially filled. This does not directly lead to symmetry breaking, but it leads to changes in certain bond lengths⁴. The non-resonant XES spectra (Fig. 2) of $V_{1.0}C_{60}$ is almost identical to that measured for the pristine C_{60} sample. Slight depletion of the E_5 spectral feature which consists mainly of ungerade states which are spectroscopically allowed to fill the (gerade) core hole (for assignment of the E_{1-5} see, e.g. ref. 5, or a related abstract⁶ in this volume). The emission spectra with detuned excitation (1.6 eV below the π^* absorption resonance), however, indicate considerably larger intensity outside the E_5 feature, which is dominant in the respective pristine C_{60} spectrum. This can be

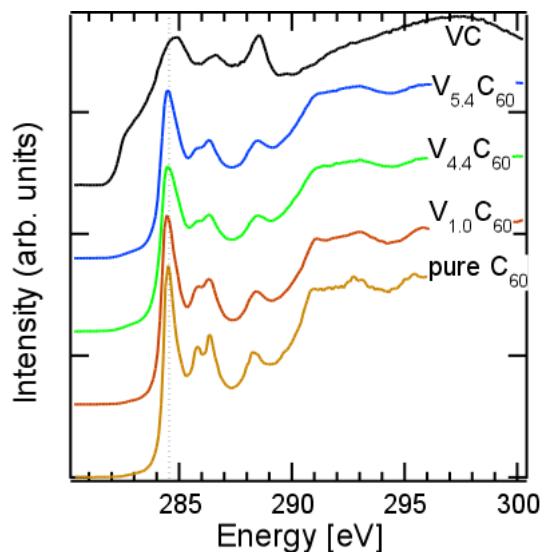


Figure 1 XAS spectra of the V_xC_{60}

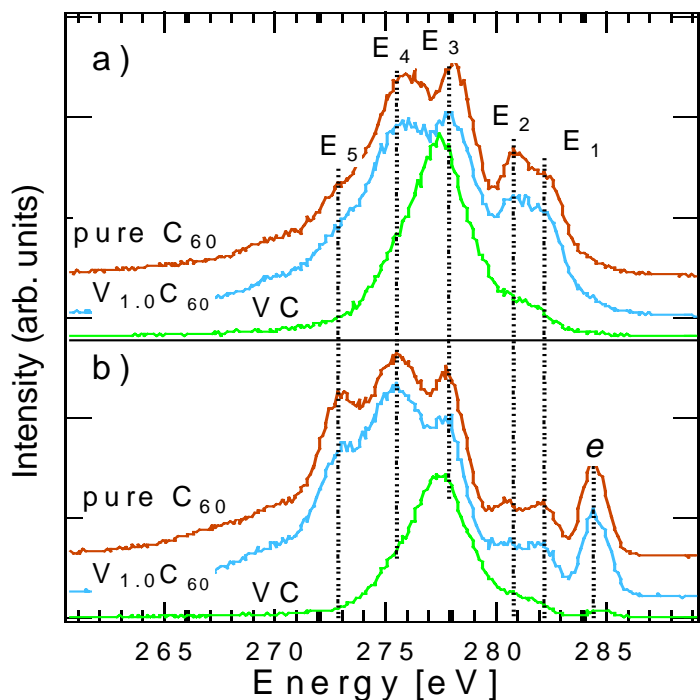


Figure 2 The a) non-resonantly and (C $1s$ -LUMO) resonantly excited X-ray emission spectra of C_{60} , $V_{1.0}C_{60}$ and VC. Excitation energies resp. 284.5 eV and 295 eV. Features E_{1-5} are explained in the text (e is elastic peak).

interpreted as a result of symmetry breaking, as E_5 is dominant in C_{60} due to symmetry reasons. The C_{60} emission bandwidth of the V_xC_{60} films is preserved throughout the excitation energy range, and the changes in spectra do not indicate uniquely carbide-like bond formation, i.e. C_{60} cage breaking (the $V_{1.0}C_{60}$ spectrum is not a composite of C_{60} and VC spectra). This can be interpreted as an indication of V_xC_{60} compound formation, with partial charge transfer towards the C_{60}^- cage.

Further experiments are planned with emission spectroscopy over a larger vanadium concentration range, to gain more understanding of the bonding mechanisms.

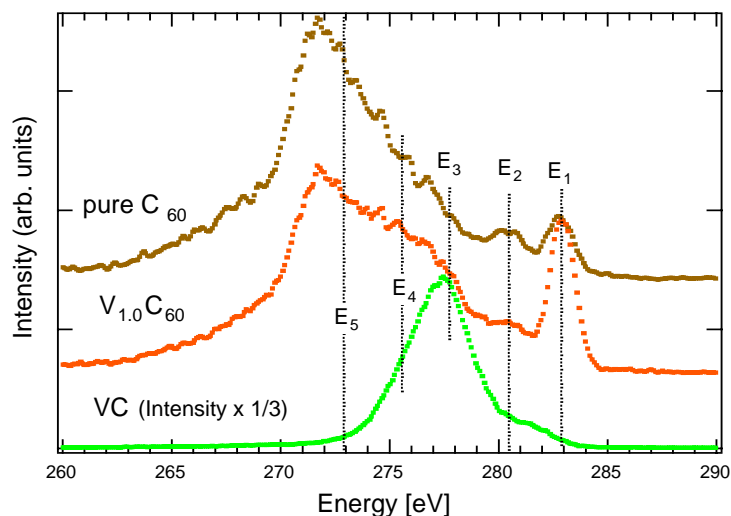


Figure 3 X-ray emission spectra, excited 1.3 eV below π^* absorption threshold (at 282.9 eV)

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